12.3; 9, 91–96°, 1.3838, 3.4; 10, 96–98°, 1.3847, 12.7; no residue.

Isopropyl alcohol, cuts 4–6, and *n*-propyl alcohol, cut 10, were identified by means of the 3,5-dinitrobenzoates; the m. p. and mixed m. p. for isopropyl derivative 120–122°; for the *n*-propyl derivative, 73°.

It was thought that cuts 8 and 9 might contain di-*n*-propyl ether, but no identification was accomplished.

The alcohol solution used to absorb propene was diluted with warm water and 34.0 g. of propene was collected. Identification of propene was made by passing the gas into sulfuric acid, diluting and distilling out isopropyl alcohol which was identified by the 3,5-dinitrobenzoate, m. p. 120–122°.

Recovery of unreacted propylamine amounted to only 0.16 mole. On the basis of 2.84 moles of unrecovered amine, the per cent. yields in the reaction were: *n*-propyl alcohol, 7.4; isopropyl alcohol, 32.0; propene, 28.4.

Summary

1. Neither methyl alcohol nor any other reaction products could be isolated from sixteen attempted reactions of monomethylamine with nitrous acid. Methylamine nitrite merely hydrolyzes into its components instead of decomposing into nitrogen and other products as do the nitrites of the higher amines.

2. Ethylamine and *n*-propylamine react with nitrous acid to yield ethanol, 1-propanol, 2-propanol and propene.

STATE COLLEGE, PENNA. RECEIVED JULY 29, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Polymerization of Olefins. III.[1] The Polymeric Olefins from Methylisopropylcarbinol

BY FRANK C. WHITMORE AND WILLIAM A. MOSHER[2]

Drake, Kline and Rose[3] studied the decenes obtained when methylisopropylcarbinol is treated with 75% sulfuric acid at 80°. They proved the presence of 3,4,5,5-tetramethyl-2-hexene (I) and 3,5,5-trimethyl-2-heptene (II); their search failed to reveal any other decenes. The first decene is an unexpected product. The fact that it was found in such a large amount, about 50% of the decenes present, in addition to its unusual nature, made further study of this reaction desirable. Moreover, a product involving a similar 1:3-shift of a methyl group had been found in this Laboratory.[1]

We have now repeated and confirmed entirely the results of the above workers. Moreover, we have obtained excellent separation of the two decenes by the use of a fractionating column of 85 theoretical plates. Drake and his co-workers studied only the decene fractions; we have in addition studied all products of the reaction.

The action of 75% sulfuric acid on methylisopropylcarbinol results in the following yields: trimethylethylene, 1%; 3-methyl-2-pentene, 3%; methyl isopropyl ketone, 1%; diisobutylenes, 1%; 2,3,4,4-tetramethyl-1-pentene, 2%; other nonenes, 1%; 3,4,5,5-tetramethyl-2-hexene (I), 45%; 3,5,5-trimethyl-2-heptene (II), 35%; higher polymers, 5%. The small amount of total intermediate materials, 5%, indicates the sharpness of the separation.

Trimethylethylene is a normal product of the dehydration of methylisopropylcarbinol. The presence of 3-methyl-2-pentene in appreciable amount is of interest. 3,4,5,5-Tetramethyl-2-hexene contains the grouping $R_3C—C—C^*$, where the asterisk indicates deficiency of an electron pair. According to the findings of Whitmore and Stahly[4] this grouping is relatively easy to depolymerize. The products of the splitting process would be 3-methyl-2-pentene and isobutylene. The first is found and the second is polymerized with itself to yield the diisobutylenes and copolymerized with trimethylethylene to yield 2,3,4,4-tetramethyl-1-pentene. The other nonenes found, 3,5,5-trimethyl-2-hexene and 2,3,4,4-tetramethyl-2-pentene, are also formed by the copolymerization process.

The presence of methyl isopropyl ketone is easily understood when it is noted that sulfur dioxide, indicating oxidation by the sulfuric acid, was always observed during the polymerization reaction.

3,5,5-Trimethyl-2-heptene (II) is formed by the union of a *t*-amyl fragment to 1,1-methylethyl-

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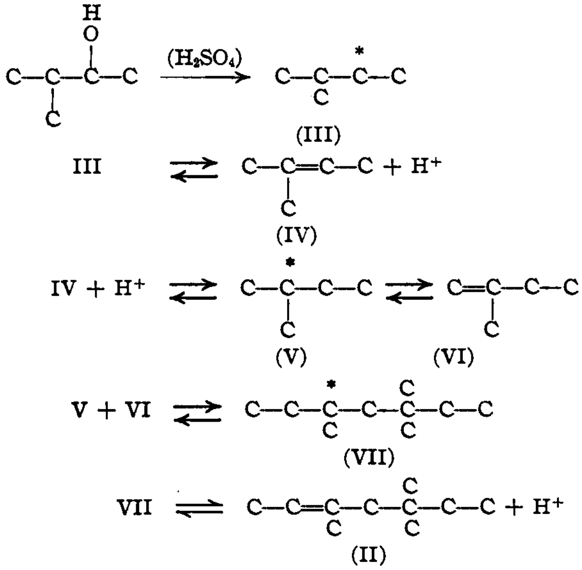
[1] For paper II of this series see THIS JOURNAL, 63, 756 (1941).

[2] Eastman Kodak Co. Research Fellow in Chemistry, 1939–1940.

[3] Drake, Kline and Rose, THIS JOURNAL, 56, 2076 (1934).

[4] Whitmore and Stahly, *ibid.*, 55, 4153 (1933).

ethylene. This reaction may be formulated as follows employing the concepts of Whitmore.[5]



The formation of II is due to the loss of a proton by the ethyl group in VII. It might be expected that two other olefins would be formed by a corresponding loss of a proton by the neohexyl group to give 3,5,5-trimethyl-3-heptene (VIII) and by the methyl group to give 2-ethyl-4,4-dimethyl-1-hexene. Neither of the last compounds could be found in spite of painstaking searches. Evidence was found that 3,5,5-trimethyl-2-heptene (II) is the only stable isomer under the conditions used. This is the first recorded case of such a difference in stability among three isomeric olefins so closely related.

The alcohol which could give 3,5,5-trimethyl-2-heptene (II) and its related isomers on dehydration, namely, 3,5,5-trimethyl-3-heptanol, was synthesized by the action of ethylmagnesium bromide on 4,4-dimethyl-2-hexanone. Dehydration of this alcohol using copper sulfate as the dehydrating agent yielded II and VIII in the ratio 6:1 as determined by ozonolysis.[6] Dehydration with 75% sulfuric acid at 80°, corresponding to the conditions under which the treatment of methylisopropylcarbinol was carried out, gave a ratio of these compounds of 20 to 1. None of the related methylene isomer was detected in either case.

The fact that 3,4,5,5-tetramethyl-3-hexene is not found while 3,4,5,5-tetramethyl-2-hexene (I) is found is probably another example of the preferential dehydration presented above. However, direct experimental evidence has not been obtained since attempts to prepare 3,4,5,5-tetramethyl-3-hexanol and 2,2,3,4-tetramethyl-3-hexanol have not yet been successful. Ethyl Grignard reagent would not add to 3,4,4-trimethyl-2-pentanone, enolization being the chief reaction[7]; the same was true of the reaction of methyl Grignard reagent and 4,5,5-trimethyl-3-hexanone.[8] The great ease with which an ethyl group has been found to lose a proton[6] fits well with the above findings as to the position of the double bonds in the decenes from methylisopropylcarbinol.

The mode of formation of 3,4,5,5-tetramethyl-2-hexene (I) will be discussed in a later paper in this series.

Experimental

Preparation of Methylisopropylcarbinol.—This alcohol was prepared by the method of "Organic Syntheses"[9] from isopropylmagnesium bromide and acetaldehyde. The carbinol of b. p. 112° (742 mm.), $n^{20}D$ 1.4092, was obtained by fractionation through a column of twelve theoretical plates.

Polymerization.—The polymerization was carried out as described by Drake, Kline and Rose.[3] No reaction took place until the mixture reached 76°, at which temperature vigorous refluxing took place. This ceased by the time the temperature reached 80°. The gas collected proved to be displaced air. The reaction mixture was cooled by the addition of ice and the crude polymer was separated, washed twice with water, twice with saturated sodium bicarbonate solution, and finally with two portions of water. The product was neutral to moist litmus paper. The refluxing with metallic sodium of Drake and his coworkers was omitted; the polymer was dried over anhydrous potassium carbonate. The yields of polymer ran from 95 to 98%.

Fractionation of the Polymer.—The first fractionation of the polymer was through Column W1[10] which was equivalent to 85 theoretical plates. The charge was 1200 g. and the fractionation was carried out at atmospheric pressure. The low-boiling materials were refractionated through a ten-plate column. Intermediate material was refractionated by parts through a thirty-plate column. Eight main fractions were thus obtained.

Identification of the Products.—With the exception of components A and C, the technique of ozonolysis was used to identify the mixtures. The methods of Whitmore and Church[11] and Church, Whitmore and McGrew[6] have been used at all times. Petroleum ether, b. p. 0–30°, was used as the solvent and the zinc–water-catalyst method of decomposition was used.

Component A, b. p. 38°, $n^{20}D$ 1.3852–1.3890, was identi-

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[5] Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

[6] Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

[7] Unpublished results of the junior author and L. H. Sutherland.

[8] Unpublished work of Dr. E. M. Jones of this Laboratory.

[9] "Organic Syntheses," Vol. XII, p. 48.

[10] This column was constructed by W. R. Wheeler of this Laboratory; it will be described in detail elsewhere.

[11] Whitmore and Church, THIS JOURNAL, **54**, 3710 (1932).

fied as trimethylethylene by treatment with bromine and the hydrolysis of the resulting dibromide to methyl isopropyl ketone.[4] The 2,4-dinitrophenylhydrazone of the methyl isopropyl ketone had a m. p. and mixed m. p. of 123°; the semicarbazone, m. p. and mixed m. p. 113°.

Component B, 68°, 1.4005 was identified as 3-methyl-2-pentene by ozonolysis. Ozonolysis of 21 g. (0.25 mole) yielded 62% acetaldehyde, isolated as the ammonia compound m. p. 96°, and 86% of methyl ethyl ketone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 113°, semicarbazone m. p. and mixed m. p. 138–139°. The amount of 3-methyl-2-pentene was 3%.

Component C, 94°, 1.3999–1.4010, was mostly methyl isopropyl ketone identified by its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 122–123°, and semicarbazone, m. p. and mixed m. p. 113°. The methyl isopropyl ketone corresponds to less than 1%.

Component D, 100–105°, 1.4120–1.4144, was identified as mainly a mixture of the two diisobutylenes. The ozonolysis of 7 g. of this material yielded 5.2 g. of oil, 0.2 g. of which boiled below 90° and gave the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. and mixed m. p. 207–209°, and the rest of the oil boiled from 120–125° and gave the derivatives of methyl neopentyl ketone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 100°, semicarbazone, m. p. and mixed m. p. 174–175°. The amount of diisobutylene was 1%.

Component E, 120–130°, 1.4175–1.4247, was a mixture of nonenes which could not be separated due to the small amount of material available. Ozonolysis of 8.5 g. yielded 5.3 g. of oil from which pinacolone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 122–124°, and methyl neopentyl ketone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 100°, were obtained. Acetaldehyde, acetone, and traces of formaldehyde were also detected. The amount of this material was about 1%.

Component F, 132–133°, 1.4275, was identified as 2,3,4,4-tetramethyl-1-pentene. Ozonolysis of 20 g. gave 10.6 g. of oil which on fractionation proved to be almost pure 3,4,4-trimethyl-2-pentanone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 112° and semicarbazone m. p. and mixed m. p. 151°.[3] Formaldehyde in an 82% yield was obtained by precipitating with dimetol (dimedone).[12] The amount of 2,3,4,4-tetramethyl-1-pentene corresponded to about 2% of the polymer.

Component G, 152°, 1.4358–1.4362, was identified as 3,4,5,5-tetramethyl-2-hexene (I). Ozonolysis of 140 g. (1 mole) yielded 0.56 mole of pure 3,4,4-trimethyl-2-pentanone, 0.62 mole of acetaldehyde, and 0.013 mole of a condensation product of the ketone. Tests for aldehyde in the water layer from the ozonolysis were negative; no acetone was found. A thorough study of all cuts from the fractionation of the ozonolysis products showed the presence of no other carbonyl compounds. The amount of 3,4,5,5-tetramethyl-2-hexene corresponded to 45% of the polymer.

Since all indications show the purity of the 3,4,5,5-tetramethyl-2-hexene its properties should be recorded, b. p. 152° at 746 mm., $n^{20}_{\rm D}$ 1.4360. About twenty fractions amounting to 250 g. were obtained with these properties through the 85-plate column.

Component H, 158°, 1.4393, was identified as 3,5,5-trimethyl-2-heptene (II). The ozonolysis of 1 mole gave 0.54 mole of 4,4-dimethyl-2-hexanone, 0.57 mole of acetaldehyde, and 0.06 mole of condensation product of the ketone. No other products were found after a careful search. About twenty fractions amounting to 175 g. of 3,5,5-trimethyl-2-heptene were obtained in apparent high purity, b. 158° at 742 mm. and $n^{20}_{\rm D}$ 1.4393. This was 35% of the polymer.

The Preparation of 3,5,5-Trimethyl-3-heptanol.—This alcohol was prepared by the action of ethylmagnesium bromide on 4,4-dimethyl-2-hexanone. The ketone was obtained by the oxidation of Sharples' Diamylene with sodium dichromate and sulfuric acid by Dr. L. H. Sutherland of this Laboratory. The ketone could not be obtained pure but formed a constant-boiling mixture with unoxidized olefin. The carbinol formed by the addition of ethyl Grignard reagent was easily separated from the olefin which contaminated the ketone. The yield of carbinol, b. p. 86° (30 mm.) $n^{20}_{\rm D}$ 1.4455, d^{20} 0.8513, molecular refraction, calcd. 49.65; found, 49.28, was 84% calculated from the actual amount of ketone reacting. The proof of the structure of this tertiary alcohol is obtained from its mode of synthesis and from the ozonolysis of its dehydration products as given below.

Dehydration of 3,5,5-Trimethyl-3-heptanol.—The carbinol was dehydrated with copper sulfate and with 75% sulfuric acid. In the first experiment 50 g. of the carbinol was dehydrated under a column which allowed the water and olefin to distill out retaining any undehydrated carbinol. The yield of olefin was 97.5%. Fractionation of the olefin through a column of fifteen plates gave no satisfactory separation of the isomers; ozonolysis was used to obtain the ratio of the isomers. Methyl ethyl ketone, 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 115°, dimethylethylacetaldehyde, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 145°, and 4,4-dimethyl-2-hexanone, semicarbazone m. p. and mixed m. p. 167°.[4] The amounts of dimethylethylacetaldehyde and 4,4-dimethyl-2-hexanone found were in the ratio of 1 to 6. Only a trace of formaldehyde was indicated by the resorcinol–sulfuric acid test.

In the second experiment 80 g. of the carbinol was dehydrated with 200 g. of 75% sulfuric acid at 80° for twenty minutes. There was no reflux during this process and nothing was caught in a dry-ice–acetone trap. Ozonolysis yielded acetaldehyde, methyl ethyl ketone, dimethylethylacetaldehyde, and 4,4-dimethyl-2-hexanone. No formaldehyde was found. The ratio of either dimethylethylacetaldehyde or methyl ethyl ketone to the 4,4-dimethyl-2-hexanone was 1 to 20.

Summary

1. The decenes obtained when methylisopropylcarbinol is treated with 75% sulfuric acid have been studied and the results of Drake, Kline and Rose confirmed.

2. Trimethylethylene, 3-methyl-2-pentene,

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(12) *Chemisches Zentralblatt* Index for 1932 gives "Dimetol, see Dimedon"; Eastman Kodak Co. Catalog calls it "dimethyldihydroresorcinol"; Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931), states "The reagent is dimethylcyclohexanedione, commonly called dimetol and dimethylhydroresorcin."

methyl isopropyl ketone, the diisobutylenes, 2,3,4,4-tetramethyl-1-pentene and other nonenes, have been found along with the chief products of the reaction, the two decenes, 3,4,5,5-tetramethyl-2-hexene and 3,5,5-trimethyl-2-heptene.

3. 3,5,5-Trimethyl-3-heptanol has been prepared and dehydrated. Dehydration with copper sulfate and with sulfuric acid give different ratios of the isomers. The relation of this dehydration to the structure of the polymers is considered.

4. Methyl and ethyl Grignard reagents would not add to 4,5,5-trimethyl-3-hexanone and 3,4,4-trimethyl-2-pentanone, respectively.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Structure and the Absorption Spectra of α,β-Unsaturated Ketones

BY ROBERT BURNS WOODWARD*

Henri,[1] working with mesityl oxide, first observed the absorption spectrum which is now accepted as characteristic in general outline of all simple α,β-unsaturated ketones. A strong absorption band ($\log \epsilon = 4.1$, $\lambda_{\text{max.}} = 236$ mμ) as well as a weak band ($\log \epsilon = 1.9$) at 315 mμ was evident. Scheibe[2] confirmed and extended this work, showing that the exact position of the wave length of maximum absorption was to some extent dependent on the solvent used. On changing to a relatively more polar solvent, the intense band was shifted toward the red, while the weak band was shifted toward the violet.

Menschick, Page and Bossert,[3] investigating cholestenone and pulegone, the latter known to be an α,β-unsaturated ketone, pointed out the similarity of the spectra of these substances to that of mesityl oxide, and adduced the resemblance as evidence of the α,β-unsaturated carbonyl character of the steroid ketone. These investigators further indicated that in general the presence of an α,β-unsaturated carbonyl system in a given compound could be correlated with intense selective absorption in the region 230–250 mμ. The anticipation that this effect would be a powerful tool in the determination of structure has been amply justified in the interim, in that the presence in a large number of compounds, of this structural feature has been adduced as a consequence of absorption in this region (*cf.* Tables II, III and IV). In the steroid series alone, more than fifty substances have been investigated, in all of which $\lambda_{\text{max.}}$ for the intense band is in the region 220–260 mμ.

In this communication it is shown that the position *within this region* of the wave length of maximum absorption may be rigidly correlated with the extent of substitution of the carbon–carbon double bond in the α,β-unsaturated carbonyl system and that consequently the determination of this physical property throws a very considerable light upon the structure of the compound under examination. In Tables II, III and IV are listed the wave lengths of maximum absorption for the intense band in the absorption spectra of all α,β-unsaturated ketones of unequivocal structure whose absorption characteristics have been measured to date. It must be emphasized that in order that the spectra of different substances shall be exactly comparable, the absorption characteristics must be determined in a single solvent, or the observed values must be corrected to a given solvent. That the mass of data now available has not previously been amenable to classification is in large part a consequence of the fact that the use of a variety of solvents for the determinations has resulted in a general diffuseness of the published values of $\lambda_{\text{max.}}$. The values of the latter in the sequel are for spectra in absolute ethanol, the published values, in case this solvent was not used, being corrected as indicated in Table I. The corrections are average values deduced from a considerable number of cases in which the shifts have been measured experimentally.[2]

TABLE I

Solvent	To correct to EtOH add
CH_3OH	−1 mμ
$CHCl_3$	±0
$(C_2H_5)_2O$	+6
Hexane	+7

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[1] Bieleski and Henri, *Ber.*, **47**, 1690 (1914).

[2] Scheibe, Rössler and Backenköhler, *ibid.*, **58**, 586 (1925).

[3] Menschick, Page and Bossert, *Ann.*, **495**, 233 (1932).